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PAPER AND METHOD OF PREPARATION

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This invention relates to improved paper products and more particularly to a method of increasing the bulk, and/or absorptive characteristics of paper and paper products.

An objective of the paper industry has long been to increase absorptiveness, and/or bulk, i.e., reduce weight while maintaining caliper or thickness, or maintain the weight while increasing caliper or thickness, of paper and paper-like products. Absorptiveness, of course, comprises an obviously advantageous characteristic in certain applications, e.g., matrix paper, while high bulk, or low weight per volume or thickness provides a conservation especially in shipping, mailing, handling or the like. Previously, characteristics such as increased bulk and/or absorptiveness have been striven for, and achieved to a degree by means of conventional types of paper fillers or pigments such as, for example, clays, talc, calcium carbonate, diatomaceous earth and the like, but it is well understood in the art that such typical fillers significantly lower sheet strength, among other disadvantages, when incorporated in substantial or effective amounts.

It is a primary object of this invention to provide a means of imparting high bulk properties, or lowweight per caliper or thickness, to paper or paper products without materially affecting the strength or other desirable and advantageous properties of such products.

It is also a primary object of this invention to provide a means of materially increasing the absorptive properties or characteristics of paper and related products which does not deleteriously affect or significantly diminish beneficial or necessary properties such as sheet strength, uniformity, etc.

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A further object of this invention is to provide a paper additament or component which imparts high bulk, or low weight per caliper or thickness and/or increases the absorptiveness of paper and paper products without materially affecting or diminishing strength, uniformity and the like desired and beneficial properties and characteristics, and additionally facilitates moisture retention and release during drying, extends the effect of opaque pigments, e.g.: titanium dioxide, thereby increasing opacity and/or reducing utilization of these costly pigments, and, among other advantages, improves ink receptivity.

It is a still further object of this invention to provide a means of, or additament which, among the hereinbefore recited objects and advantages, favorably influences smoothness, shrinkage, porosity and freeness as well as producing an alkaline furnish and thereby reducing corrosion of equipment and permitting the use of low cost alkaline fillers such as calcium carbonate.

Further objects and advantages of this invention will become apparent and more fully understood from the hereinafter detailed description.

This invention involves a novel and improved, water insoluble, synthetic hydrated calcium silicate additament or paper component as a means of effecting bulking and/or absorptiveness, among other properties, in paper and paper products. The insoluble particulate calcium silicates of this invention comprise only those prepared by hydrothermal reaction (i.e., chemical reaction in the presence of water at elevated temperatures) of an aqueous suspension or slurry of lime and a siliceous material, such as diatomaceous earth,

silicic acid, tripolite, quartz or the like, at temperatures of at least 65°C., preferably approximately 100 to 260°C., for periods of at least 20 minutes, preferably greater. The reaction time, however, varies in proportion to the temperature, i.e., approximately 20 minutes or more at temperatures in the range of about 175 - 260°C. up to several hours or even days at minimum temperatures may be required to complete the reaction. One suitable hydrated calcium silicate product for practice of this invention and a typical method of preparing the same is described in United States Letters Patent No. 1,574,363 to Calvert. The hydrated calcium silicate of this patent is known in the art as calcium silicate hydrate I, a compound of variable composition having a CaO/SiO_2 mol ratio of 0.8 to 1.5 of lime to 1 of silica which has been described in detail by Taylor, Journal of the Chemical Society, 163 (1950). Of course other hydrated calcium silicate compositions of equivalent quality may be prepared hydrothermally, for example, xonotlite, a hydrated calcium silicate having the molecular composition $5CaO.5SiO_2.H_2O$ or the calcium silicate compound described in copending Canadian application, Serial No. 727,526, filed April 18, 1957, now Canadian Patent No. 601,158 issued July 5, 1960, and as such are equally applicable in the practice of this invention. The preferred hydrated calcium silicate compound comprises the hydrothermal batch reaction product of an aqueous suspension of lime and diatomaceous silica having a mol ratio within the range of 0.05 - 0.7 CaO to 1 SiO_2, and preferably approximately 0.5, at a temperature of about 450°F. for approximately 2 hours, a particulate calcium silicate product having a composition $2CaO.3SiO_2.1\text{-}2.5H_2O$ and more fully identified in the aforementioned copending application Serial No. 727,526, now Canadian Patent No. 601,158, and

characterized by a unique X-ray diffraction pattern having very strong lines d = 3.12Å and d = 4.12Å and a medium line line at d = 8.34Å.

Hydrated calcium silicates thus prepared exhibit low wet densities, for example, typically less than about 12 to 14 lbs. per cubic foot, whereas the common natural calcium silicates contemplated or those comprising the precipitated reaction product of combining a soluble calcium compound such as calcium chloride and a soluble silicate such as sodium silicate exhibit relatively high wet densities such as about 18 lbs. per cubic foot or greater for the synthetically precipitated calcium silicates. Thus, without limiting this invention to any particular theory, but for the purposes of explanation and illustration, rather than limitation, observations and deductions indicate that among all the other properties and/or characteristics differentiating hydrothermally prepared hydrated calcium silicates from those produced by unlike means, it is primarily the low wet density of the hydrothermally prepared products which effects the desirable and beneficial results provided by this invention. Accordingly, the novel and advantageous paper additament or component of this invention must comprise a particulate hydrated calcium silicate product which is produced by hydrothermal chemical reaction of lime and a siliceous component, that is, one exhibiting a low wet density of at most about 12 to 14 lbs. per cubic foot, preferably approximately 12 lbs. per cubic foot or less.

The hydrated calcium silicates of this invention are incorporated in paper or paper products in amounts ranging from approximately 1 to 30%, based upon the dry weight of the paper, and depending, of course, upon the nature and/or extent of the properties or characteristics desired, i.e., bulk and/or absorptiveness among other properties or characteristics imparted by this invention in addition to those typical of paper, and the type or class of paper and manufacturing techniques. Preferably, at least about 2% and typically approximately 5 to 15% of a hydrated calcium silicate, based upon the dry weight of the paper, satisfies most applications. Of course, the hydrated calcium silicate must be in fine particulate or powdered form of a size classification within the approximate range of typical clay and the like paper fillers and pigments for addition to most typical papers or paper products, and particle sizes of about 95% less than 40 microns have been found appropriate, rendering papers uniform and free from cuts, breaks, spots, marks, etc. Further, the particulate calcium silicate may be added to or combined with the paper forming slurry or stock at substantially any conventional process stage, preferably at or during heating.

The following example illustrates a method or means of imparting bulk and/or absorptiveness to papers in accordance with this invention. It is to be understood that papers or their components and the particulate calcium silicate are exemplary and are not to be construed to limit the method or meansto any particular paper, paper product or typical component thereof specified in the hereinafter example other than the hydrated calcium silicate which exhibits wet density not exceeding about 12 to 14 lbs. per cubic foot.

A base stock comprising methylated cotton linter pulp was prepared by heating for 2-1/2 hours in a conventional paper beater. Ten samples were prepared using 100% of this cotton pulp base stock and a second similar set of 10 samples was made by including 10% by weight of a hydrated calcium silicate comprising the hydrothermal reaction product of an aqueous suspension of lime and diatomaceous silica in a mol ratio of 0.5 at about 450°F. for approximately 2 hours and having a wet density of about 9 lbs. per cubic foot. Sheets were prepared by pressing on a hand-sheet press at uniform pressure and the basic weights of the sheets were approximately 14 pounds per 100 square feet.

Weight and thickness tests were obtained on each sample. Tensile strips were 12" x 1" and tested with a ten inch clearance between the jaws. Internal tear strength was obtained on the Elmendorf tear tester. Absorptiveness was obtained in water and penetration rate was measured using water. Air resistance was measured on a Gurley densometer and is recorded in seconds per 100 cc. All tests were made on an oven dry basis.'

The physical properties of straight fiber paper and hydrated calcium silicate containing paper are as follows:

PHYSICAL PROPERTIES OF HANDSHEETS CONTAINING HYDRATED CALCIUM SILICATE

	Paper comprising 100% Fiber (Control)	Paper containing 10% Calcium Silicate
Weight (lb./sq. ft.)	.149	.143
Ream weight 24x36x480 (lbs.)	428	413
Thickness (in.)	.0395	.0466
Density (lb./cu. ft.)	45.4	36.9
Tensile (p.s.i.)	3870	3750
Tear (gms.)	1354	1126
Tear (gms. lb.)	9080	7870
Gurley Densometer (Sec./100 cc.)	28	15
Water Absorption - 1/2 hr. (%)	156	191
Penetration Time (Water) (Sec.)	340	158
Ash Content (%)	.36	9.26
Stock Freeness (cc.)	325	320

The handsheets containing hydrated calcium silicates are substantially low in density, and absorptive capacity is materially improved over the control. This increase in bulk and other properties is accompanied only by a slight decrease in tensile and tear strength. Penetration time of water was twice as fast on the sheets containing the hydrated calcium silicate and the densometer reading was one-half that of the control sheets. Ash tests indicate that retention of the hydrated calcium silicates was approximately 90%.

The method of this invention is applicable to the manufacture of numerous classes of paper, paper specialties and paper products. For example, the desirable and beneficial properties and characteristics imparted by this invention render it desirable in the manufacture of magazine

writing, wrapping and the like paper where mailing and handling costs are a substantial consideration, and in the manufacture of matrix, blotting, towel and similar absorbent papers wherein improved water or the like absorbency as well as strength and plasticity are essential. Further, the specific properties and characteristics resulting from or enhanced by this invention renders the same particularly useful in the manufacture of matrix papers.

The hydrothermally prepared hydrated calcium silicates described hereinbefore — that is hydrated calcium silicate compounds having low wet densities typically less than about 12 to 14 lbs. per cubic foot — may, if desired or appropriate, be treated with alum (sulfates of aluminum and/or iron) prior to introduction into the paper slurry, or they may be added to a paper slurry containing substantial, but conventional, amounts of alum. Alum treatment, i.e., reaction between the calcium silicate and a sulfate or sulfates of aluminum and/or iron, among other advantages, reduces the extent of subsequent reaction between the calcium silicate and alum frequently present in many typical paper slurries.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of bulking and increasing absorptiveness of paper which comprises incorporating therein approximately 1 to 30%, based upon the dry weight of the paper, of particulate hydrated calcium silicate having a wet density not exceeding about 14 pounds per cubic foot and consisting essentially of the hydrothermal reaction product of an aqueous suspension of lime and a siliceous material in a CaO/SiO_2 mol ratio of between approximately 0.1 and 0.7 to 1 at a temperature of approximately 182 to 260°C. for a period of at least approximately 20 minutes.

2. A method of bulking and increasing absorptiveness of paper which comprises incorporating therein approximately 1 to 30%, based upon the dry weight of the paper, of particulate hydrated calcium silicate having a wet density not exceeding about 14 pounds per cubic foot and consisting essentially of the hydrothermal reaction product of an aqueous suspension of lime and a siliceous material in a CaO/SiO_2 mol ratio of between approximately 0.5 to 1 at a temperature of approximately 182 to 260°C. for a period of at least approximately 20 minutes.

3. A method of bulking and increasing absorptiveness of paper which comprises incorporating therein approximately 1 to 30%, based upon the dry weight of the paper, of particulate hydrated calcium silicate consisting essentially of the hydrothermal reaction product of an aqueous suspension of lime and a siliceous material in a

CaO/SiO_2 mol ratio of between approximately 0.3 and 1.5 to 1 at a temperature of approximately 100 to 260°C. for a period of about 2 hours.

4. A method of bulking and increasing absorptiveness of paper which comprises incorporating therein approximately 2 to 30%, based upon the dry weight of the paper, of particulate hydrated calcium silicate having a wet density not exceeding about 12 pounds per cubic foot and consisting essentially of the hydrothermal batch reaction product of an aqueous suspension of lime and a siliceous material in a CaO/SiO_2 mol ratio of between approximately 0.1 and 0.7 to 1 at a temperature of approximately 235°C. for a period of about 2 hours.

5. A method of bulking and increasing absorptiveness of paper which comprises incorporating therein approximately 2 to 30%, based upon the dry weight of the paper, of particulate hydrated calcium silicate having a wet density not exceeding about 12 pounds per cubic foot and consisting essentially of the hydrothermal batch reaction product of an aqueous suspension of lime and a siliceous material in a CaO/SiO_2 mol ratio of between approximately 0.5 to 1 at a temperature of approximately 235°C. for a period of about 2 hours.

6. A method of bulking and increasing absorptiveness of matrix paper which comprises incorporating therein approximately 2 to 30%, based upon the dry weight of the matrix, of particulate hydrated calcium silicate having a wet density not exceeding about 12 pounds per cubic foot

and consisting essentially of the hydrothermal batch reaction product of an aqueous suspension of lime and a siliceous material in a CaO/SiO_2 mol ratio of between approximately 0.1 and 0.7 to 1 at a temperature of approximately 235°C. for a period of about 2 hours.

7. A method of bulking and increasing absorptiveness of matrix paper which comprises incorporating therein approximately 2 to 30%, based upon the dry weight of the matrix, of particulate hydrated calcium silicate having a wet density not exceeding about 12 pounds per cubic foot and consisting essentially of the hydrothermal batch reaction product of an aqueous suspension of lime and a siliceous material in a CaO/SiO_2 mol ratio of between approximately 0.5 to 1 at a temperature of approximately 235°C. for a period of about 2 hours.

8. A high bulk and absorbent paper product comprising from approximately 1 to 30%, based upon the dry weight of the paper product, of particulate hydrothermally reacted calcium silicate dispersed throughout.

9. A high bulk and absorbent paper product comprising from approximately 1 to 30%, based upon the dry weight of the paper product, of particulate hydrothermally reacted calcium silicate consisting essentially of calcium silicate hydrate I having a wet density not exceeding about 14 pounds per cubic foot dispersed throughout.

10. A high bulk and absorbent paper product comprising from approximately 1 to 30%, based upon the dry weight of the paper product, of particulate hydrothermally reacted calcium silicate consisting essentially of the hydrated calcium silicate xonotlite dispersed throughout.

11. A high bulk and absorbent paper product comprising from approximately 1 to 30%, based upon the dry weight of the paper product, of particulate hydrothermally reacted calcium silicate having a wet density not exceeding about 12 pounds per cubic foot consisting essentially of the hydrated calcium silicate $2CaO.3SiO_2.1\text{-}2.5H_2O$ which is characterized by a unique X-ray diffraction pattern having very strong lines d = 3.12Å and d = 4.12Å and a medium line d = 8.34Å dispersed throughout.

12. A high bulk and absorbent paper product comprising from approximately 2 to 30%, based upon the dry weight of the paper product, of particulate hydrothermally reacted calcium silicate having a wet density not exceeding about 12 pounds per cubic foot and consisting essentially of the hydrated calcium silicate $2CaO.3SiO_2.1\text{-}2.5H_2O$.

13. A method of bulking and increasing absorptiveness of paper which comprises incorporating therein approximately 1 to 30%, based upon the dry weight of the paper, of a particulate hydrated calcium silicate having a wet density not exceeding about 14 pounds per cubic foot and consisting essentially of $2CaO.3SiO_2.1\text{-}2.5H_2O$ which is characterized by a unique X-ray diffraction pattern having very strong lines d = 3.12Å and d = 4.12Å and a medium line at d = 8.34Å.

14. A method of bulking and increasing absorptiveness of paper which comprises incorporating therein approximately 1 to 30%, based upon the dry weight of the paper, of a particulate hydrated calcium silicate having a wet density not exceeding about 14 pounds per cubic foot and consisting essentially of $2CaO.3SiO_2.1\text{-}2.5H_2O$ which is characterized by a unique X-ray diffraction pattern having very strong lines d = 3.12Å and d = 4.12Å and a medium line at d = 8.34Å and comprises the reaction product of an aqueous slurry of lime and a siliceous material in a CaO/SiO_2 mol ratio of 0.1 - 0.7CaO to 1 SiO_2 at a temperature of at least approximately 182°C.

15. A method of bulking and increasing absorptiveness of paper which comprises incorporating therein approximately 1 to 30%, based upon the dry weight of the paper, of a particulate hydrated calcium silicate having a wet density not exceeding about 12 pounds per cubic foot and consisting essentially of $2CaO.3SiO_2.1\text{-}2.5H_2O$ which is characterized

by a unique X-ray diffraction pattern having very strong lines d = 3.12Å and d = 4.12Å and a medium line at d = 8.34Å and comprises the reaction product of an aqueous slurry of lime and a siliceous material in a CaO/SiO_2 mol ratio of 0.5 CaO to 1 SiO_2 at a temperature of at least approximately 182°C.

16. A method of bulking and increasing absorptiveness of paper which comprises incorporating therein approximately 1 to 30%, based upon the dry weight of the paper, of a particulate hydrated calcium silicate having a wet density not exceeding about 14 pounds per cubic foot and consisting essentially of calcium silicate hydrate I which comprises the reaction product of an aqueous slurry of lime and siliceous material in a CaO/SiO_2 mol ratio of approximately 0.8 - 1.5 CaO to 1 SiO_2 at a temperature of at least approximately 65°C. up to approximately 175°C. for a period of at least approximately 20 minutes to effect substantial reaction between said lime and siliceous material.

17. A method of bulking and increasing absorptiveness of paper which comprises incorporating therein approximately 1 to 30%, based upon the dry weight of the paper, of a particulate hydrated calcium silicate having a wet density not exceeding about 14 pounds per cubic foot and consisting essentially of calcium silicate hydrate I which comprises the reaction product of an aqueous slurry of lime and siliceous material in a CaO/SiO_2 mol ratio of approximately 0.8 - 1.5 CaO to 1 SiO_2 at a temperature of approximately 100 - 175°C. for a period of at least approximately 20 minutes to effect substantial reaction between said lime and siliceous material.